



Soil phosphorus fractions in solution: influence of fertiliser and manure, filtration and method of determination

Richard W. McDowell, Andrew N. Sharpley *

USDA-ARS, Pasture Systems and Watershed Management Unit, Curtin Road, University Park, PA 16802-3702, USA

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Abstract

This study investigated the forms of soil P released to solution, accuracy of their determination, and influence of colloids on P sorption/desorption dynamics. A Hagerstown silt loam, amended with dairy and poultry manure or superphosphate at five rates (0, 25, 50, 100, and 200 kg P ha⁻¹), was extracted at two soil:solution ratios (1:5 and 1:100) and filtered at three pore sizes (0.8, 0.45, and 0.22 µm). Results showed that relative to the proportion of dissolved organic P (DOP, determined as the difference between total dissolved P [TDP] and P detected by ion chromatography), DRP increased with amendment rate. Relative to Mehlich-3 extractable P, DRP exhibited a power relationship with a much greater potential for soil P release at concentrations in excess of ca. 50 mg Mehlich-3 P kg⁻¹. Concentrations of DRP, determined by the acid molybdate method, were on average 12.5% greater than P detected by ion chromatography indicating P was solubilised during colorimetric determination. A linear relationship was found between total Al and DRP, which could indicate acid mediated hydrolysis of Al–humic–P substances, although acid mediated desorption of P from colloids cannot be discounted. No difference in solubilised P was found between solutions filtered at 0.22 and 0.45 µm, but was found between 0.8 µm and smaller filter sizes. Organic P extracted from manured soils was more recalcitrant than that extracted from soils amended with superphosphate, the later attributed to its accumulation in more labile pools. The sorption/desorption of P by colloids in solution were greatly affected by the rate of amendment and the soil:solution extraction ratio. More P was sorbed by superphosphate solutions compared to dairy manure amended soil solutions and was attributed to the saturation of colloidal P sorption sites by organic matter. In order to minimise the effects of colloids on P dynamics and the potential for hydrolysis in solution, filtration to at least 0.45 µm is required. However, soils with a lesser aggregate stability may require additional filtration. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phosphate; Soil solution; Analysis; Filtration; Manure; Fertiliser

1. Introduction

A significant proportion of phosphorus (P) in soil, soil solution, overland flow, and subsurface drainage can be in organic forms (Smith and Jackson, 1998;

Turner and Haygarth, 2000a). While dissolved inorganic P is important for plant uptake, a proportion of dissolved organic P can also be utilised (Turner and Haygarth, 2000b).

Soil has a strong affinity for P, however, movement of P in overland flow and subsurface drainage waters occurs. Losses of P are related to soil P concentration and, therefore, strongly influenced by P additions of fertilisers and manures (McDowell et al., 2001). Manure and slurry can contain a significant proportion of total P as organic P forms. Some of these organic P forms are

* Corresponding author. Tel.: +1-814-865-5572; fax: +1-814-865-2058.

E-mail address: ans3@psu.edu (A.N. Sharpley).

stable and relatively mobile in soil (Frossard et al., 1989). Hence, relative to the quantity of P applied, fertilisers and manures can have very different P concentrations in runoff and leachate.

Studies that have examined the importance of organic P movement from soils often quantify this fraction as the difference between orthophosphate as detected by the colorimetric acid molybdate method of Murphy and Riley (1962) before and after digestion (e.g., Chardon et al., 1997). However, it is recognised that this method is subject to a number of interferences. These include the acid mediated hydrolysis of dissolved compounds by the reagent during the formation of the blue colouration and the over- or underestimation of orthophosphate caused by the presence of nitrate, arsenate, silicate, fluoride ions, or organic compounds such as acetate, oxalate, citrate, and humic substances (Ciavatta et al., 1990; Gerke, 1992; Blomqvist et al., 1993; Cai et al., 1994). In addition to these interferences are those caused by colloids in solution. To minimise these, solutions are commonly filtered through a cellulose nitrate filter ($<0.45\ \mu\text{m}$) (Ron Vaz et al., 1993; Haygarth et al., 1995). However, a significant amount of smaller colloidal particles such as Al and Fe oxides, oxyhydroxides, and humic substances are not excluded (Gerke and Jungk, 1991; Aiken and Jeenher, 1993; Sinaj et al., 1998). These colloids could both sorb P from solution or serve as sources of P via acid mediated desorption. However, true determination of orthophosphate can be achieved by ion chromatography (Denison et al., 1998).

Our objectives were threefold:

- To determine the relative influence of inorganic fertiliser, poultry manure, and dairy manure at five rates on soil solution P fractions. Two different soil:water ratios were used designed to mimic sediment to solution ratios, and estimate P lost in subsurface drainage waters (1:5) and overland flow (1:100), respectively (McDowell and Sharpley, 2001a).
- To quantify orthophosphate and therefore organic P (by difference from total P) in these solutions using ion chromatography and colourimetric methods to estimate the influence of acid mediated hydrolysis, interferences, and/or P desorption from particulates (<0.8 , <0.45 , and $<0.22\ \mu\text{m}$).
- Examine the effect of colloids on P sorption after filtration of solutions at either 0.8, 0.45, or $0.22\ \mu\text{m}$, which represent common definitions of soluble reactive P (SRP, $<0.8\ \mu\text{m}$) and dissolved reactive P (DRP, <0.45 and $0.22\ \mu\text{m}$), and adding a range of known P concentrations.

It must be mentioned that while the three objectives valuable information for the environmental analysis and potential management of a soil a major constraint in our study lies in the use of only one soil type, and therefore a lack of comparable data.

2. Materials and methods

2.1. Soils

The soil is a fine, mixed, mesic Hagerstown silt loam (Typic Hapludalf) under perennial ryegrass (*Lolium perenne* L.). The Hagerstown soil used had a clay content of 19%, organic C concentration of $21.7\ \text{g kg}^{-1}$, and pH of 6.5. Inorganic fertiliser (as triple superphosphate, referred to here as 'superphosphate'), and poultry and dairy manure were applied in the spring of each year for five years at rates of 0, 25, 50, 100, and $200\ \text{kg P ha}^{-1}$ to 2 m diameter plots. Topsoil samples (0–5 cm depth) were taken in June 2000, air-dried, sieved ($<2\ \text{mm}$), and stored until used here.

2.2. Soil extraction and analysis

Air-dried soils were analysed in triplicate for Mehlich-3 extractable P (Mehlich, 1984). In addition, duplicate samples of each soil (15 in total, including amended and unamended soils) were shaken for 30 min in distilled water at soil:solution ratios of 1:5 or 1:100. The soil extracts were then centrifuged (3 min at 3000 rpm) and filtered at either 0.8, 0.45, or $0.22\ \mu\text{m}$ using cellulose-nitrate filters of a 47 mm diameter that were changed if necessary every 30 s to maintain a constant flow rate.

To assess the influence of colloidal materials on P concentrations, 3 l of water extract were obtained for each of the 90 solutions (one replicate of the 15 soils, two ratios and three filtration sizes). 50 ml of extract from each treatment were spiked with P (as KH_2PO_4) to give final solution concentrations of 0, 0.25, 0.5, 1.0, and $2.5\ \text{mg l}^{-1}$, excluding the concentration of P already present in the sample. After 16 h of equilibration, the spiked samples were analysed using ion chromatography and manually (detection limit $0.01\ \text{mg P l}^{-1}$) using the method of Murphy and Riley (1962). Total P in the spiked samples was also determined manually after Kjeldhal digestion (Taylor, 2000). Fractions of P were then operationally defined as:

- Orthophosphate = P detected by ion chromatography (IC).
- Dissolved reactive P (DRP) = P determined by the method of Murphy and Riley.
- Total dissolved P (TDP) = P determined by the method of Murphy and Riley following Kjeldahl digestion.
- Unreactive P (UP) = $\text{TDP} - \text{DRP}$.
- Dissolved organic P (DOP) = $\text{TDP} - \text{P detected by ion chromatography}$.
- % solubilised P = $(\text{DRP} - \text{P (by IC)}) / \text{DOP} \times 100$.

Orthophosphate determinations by ion chromatography were performed using a Lachat system with an anion guard column (Lachat part no. 28085) and a

profiling column (Lachet part no. 28084). Sample volumes of 0.1 ml were injected and eluted with NaHCO_3 (adjusted to pH 8.0 with HCl) at a flow rate of 1 ml min^{-1} . Phosphorus was eluted after 20 min, the machine washed with eluent and re-equilibrated before the next sample was introduced. This method had a detection limit of 0.1 mg P l^{-1} .

Digested samples without added orthophosphate spikes were also analysed for Al, Ca, Fe, and Mg by inductively coupled plasma – mass adsorption spectroscopy.

2.3. Statistical analyses

Statistical comparisons of soil solution fractions were calculated by an analysis of variance. The data for the three manure types were analysed separately to test the effect of manure application rate, soil:solution extraction ratio, and filter size on the concentration of P in each P fraction. A preliminary analysis of variance showed that there was no significant effect of filter size on the distribution of P in each P fraction (except for % solubilised P). Similarly, the effect of manure rate and soil:solution ratio on P in each fraction was tested. If an *F*-test proved significant at $P < 0.05$ for each factor, then means were compared using Tukey's test at the same level of significance (Snedecor and Cochran, 1991).

To determine the effects of sorption on the spiked samples, standardised data (to a solution concentration of $0\text{--}2.5 \text{ mg P l}^{-1}$) were fitted to the Freundlich isotherm ($P \text{ sorbed} = \alpha c^\beta$, where c is the concentration of P in solution and α and β are constants), and a one-way analysis of variance was run on the constants α and β . The Freundlich constants α and β are correlated to the Langmuir measures of P sorption maximum and affinity parameters, respectively (Holford, 1982). Again where an *F*-test proved significant, means were compared by Tukey's test at the same level of significance. All statistical analyses and curve fits were done with SPSS v10.0 (SPSS Inc., 1999).

3. Results

3.1. Solution P fractions

There was a wide range in soil extract P concentration within each of the P fractions (Tables 1–3). On average, DRP concentrations for all solutions were linearly correlated with TDP ($r = 0.994$), making up 81% of TDP. However, DRP accounted for a greater proportion of TDP as more P was applied. For example, DRP makes up only ca. 10% of TDP for those soils with no P applied and nearly 90% of TDP for the soil with 200 kg P ha^{-1} of dairy manure applied (Tables 1–3). The opposite trend occurred for

both DOP and UP. However, DOP concentration increased with P application and was most affected by dairy manure > poultry manure > superphosphate.

Analysis of variance indicated that significantly ($P < 0.05$) greater P concentrations in each fraction was extracted at a soil:solution ratio of 1:5 than 1:100 (Tables 1–3). Also, the concentration of P extracted, increased with P application ($P < 0.05$) for each soil:solution ratio and amendment type. However, the relationship between soil:solution ratio and the quantity of P extracted is non-linear due to the soils buffering capacity, and consequently the 1:5 ratio did not result in a concentration 20 times that of the 1:100 ratio.

Relative to Mehlich-3 extractable P (Table 4), DRP increased in a non-linear fashion in those soils extracted at a 1:5 soil:solution ratio. However, the relationship was linear for soils extracted at a soil:solution ratio of 1:100 and amended with either poultry manure or superphosphate, although more variance was accounted for by a power relationship for soil treated with dairy manure (Fig. 1). In contrast to DRP, TDP extracted at both ratios was linearly related to Mehlich-3 extractable P ($R^2 = 0.852\text{--}0.998$; data not presented).

Solution P concentrations were not related to extractable Ca or Mg. However, concentrations of Al and Fe in solution for each filtration size and amendment rate were related to P concentration (Fig. 2). For extractable Al (determined by ICP-MAS), two distinct relationships with DRP (determined manually) were obtained for those soils that had received dairy manure and another for soils that had received poultry manure or superphosphate (Fig. 2). Concentrations of Fe were also related to P in solution (Fig. 2), although unlike Al, no data separation among treatment types was noted.

3.2. Method of analysis

Slope of the regression line between the concentration of each dissolved P fraction was used here as a criterion to indicate their relative response to changes in TDP concentration (McDowell and Condron, 2000). The slope of DRP, UP, and DOP against TDP was 0.88, 0.12, and 0.20, respectively. If no solubilisation of P (acid mediated hydrolysis or desorption from colloids) had occurred, the sum of DOP plus DRP (both determined manually) should equal 1. This was not the case.

Analysis of variance indicated that there was no significant difference in the percentage of solubilised P between the two extraction ratios. Thus the data for both ratios were pooled and showed that a significant difference was evident between the proportion of P solubilised at each amendment rate. Subsequent analysis

Table 1

Mean concentrations of P fractions in solutions extracted from soils with dairy manure applied

Manure rate (kg P ha ⁻¹)	Filter pore size (µm)	DRP (mg l ⁻¹)	UP (mg l ⁻¹)	DOP (mg l ⁻¹)	Total P (mg l ⁻¹)
<i>1:5 soil:solution ratio</i>					
0	0.8	0.021† ^a	0.080†	— ^b	0.101†
	0.45	0.015†	0.068†	—	0.073†
	0.22	0.017†	0.067†	—	0.084†
25	0.8	0.028†	0.098†	—	0.126†
	0.45	0.015†	0.279‡	0.283‡	0.293‡
	0.22	0.027†	0.051†	—	0.078†
50	0.8	0.540‡	0.077†	0.257‡	0.617‡
	0.45	0.477‡	0.100†	0.238‡	0.578‡
	0.22	0.420‡	0.090†	0.251‡	0.511‡
100	0.8	0.962§	0.230‡	0.472‡	1.192‡
	0.45	0.921§	0.247‡	0.418‡	1.168‡
	0.22	0.921§	0.271‡	0.422‡	1.192‡
200	0.8	4.756¶	0.433§	0.799§	5.189§
	0.45	4.661¶	0.600§	0.711§	5.261§
	0.22	4.708¶	0.600§	0.728§	5.308§
<i>1:100 soil:solution ratio</i>					
0	0.8	0.033†	0.018†	—	0.049†
	0.45	0.012†	0.050†	—	0.062†
	0.22	0.013†	0.062†	—	0.075†
25	0.8	0.070‡	0.065†	—	0.136†
	0.45	0.071‡	0.060†	—	0.131†
	0.22	0.067‡	0.073†	—	0.140†
50	0.8	0.186§	0.043†	0.149†	0.229‡
	0.45	0.181§	0.043†	0.115†	0.225‡
	0.22	0.187§	0.050†	0.137†	0.237‡
100	0.8	0.282¶	0.046†	0.158†	0.328‡
	0.45	0.264¶	0.015†	0.040†	0.280‡
	0.22	0.262¶	0.037†	0.099†	0.299‡
200	0.8	1.155*	0.436‡	0.581‡	1.591§
	0.45	1.135*	0.330‡	0.395‡	1.465§
	0.22	1.131*	0.454‡	0.555‡	1.585§

^a Means for each application rate within a column and soil:solution ratio followed by the same letter are not significantly different at the $P < 0.05$ level using Tukey's test.

^b Undetermined due to small concentration of orthophosphate at or less than detection limit of IC.

within each amendment rate indicated that the proportion of P solubilised after filtration at <0.8 µm was significantly different to that after filtration at either <0.45 or <0.22 µm.

In general, the proportion of solubilised P decreased with amendment rate in those soils treated with dairy manure, and to a lesser degree with poultry manure. However, the opposite occurred in those soils treated with superphosphate (Table 5). On average, the manual method of Murphy and Riley (1962) detected 12.5% more P than by ion chromatography (P determined by ion chromatography = $0.875 \times$ P determined by colourimetry, $R^2 = 0.96^{***}$). While the difference may not be much in terms of DRP or TDP, solubilised P (as desorption of P from colloids and/or the hydrolysis of organic P) ranged from 16% to 73% of DOP (Table 5).

3.3. Sorption of P in solution

Analysis of variance indicated that the Freundlich parameter α (used here as an indicator for P sorption, Holford, 1982) was affected by each amendment type ($P < 0.05$). Within each manure type, P sorption in solution was affected by the soil:solution ratios during extraction and within each ratio by the rate of application. However, no affect of filter size could be determined. Those significant differences found paralleled those evident for DRP (Tables 1–3), and are therefore not shown here for brevity. In contrast to α , the Freundlich parameter β (used here as an indicator of the strength of P sorption or P affinity; Holford, 1982), showed no trend for any significant differences among amendment type and rate, soil:solution ratio, or filter pore size.

Table 2

Mean concentrations of P fractions in solutions extracted from soils with poultry manure applied

Manure rate (kg P ha ⁻¹)	Filter pore size (µm)	DRP (mg l ⁻¹)	UP (mg l ⁻¹)	DOP (mg l ⁻¹)	Total P (mg l ⁻¹)
<i>1:5 soil:solution ratio</i>					
0	0.8	0.017 ^{†a}	0.081 [†]	– ^b	0.098 [†]
	0.45	0.014 [†]	0.068 [†]	–	0.072 [†]
	0.22	0.017 [†]	0.077 [†]	–	0.094 [†]
25	0.8	0.026 [†]	0.332 [‡]	0.338 [†]	0.358 [‡]
	0.45	0.013 [†]	0.333 [‡]	0.336 [†]	0.346 [‡]
	0.22	0.010 [†]	0.198 [†]	0.202 [†]	0.202 [‡]
50	0.8	0.298 [‡]	0.136 [†]	0.384 [†]	0.434 [‡]
	0.45	0.203 [‡]	0.105 [†]	0.209 [†]	0.309 [‡]
	0.22	0.163 [‡]	0.184 [†]	0.297 [†]	0.347 [‡]
100	0.8	1.188 [§]	0.066 [†]	0.274 [†]	1.254 [§]
	0.45	1.150 [§]	0.253 [†]	0.873 [‡]	1.403 [§]
	0.22	0.861 [§]	0.221 [†]	0.322 [†]	1.082 [§]
200	0.8	2.691 [¶]	0.322 [‡]	0.653 [‡]	3.013 [¶]
	0.45	2.521 [¶]	0.340 [‡]	0.621 [‡]	2.861 [¶]
	0.22	2.492 [¶]	0.353 [‡]	0.616 [‡]	2.846 [¶]
<i>1:100 soil:solution ratio</i>					
0	0.8	0.023 [†]	0.038 [†]	–	0.061 [†]
	0.45	0.014 [†]	0.048 [†]	–	0.052 [†]
	0.22	0.013 [†]	0.065 [†]	–	0.078 [†]
25	0.8	0.183 [‡]	0.052 [†]	–	0.275 [‡]
	0.45	0.176 [‡]	0.078 [†]	–	0.235 [‡]
	0.22	0.141 [‡]	0.116 ^{‡§}	–	0.254 [‡]
50	0.8	0.195 [§]	0.042 [†]	0.057 [†]	0.257 [‡]
	0.45	0.199 [§]	0.035 [†]	0.044 [†]	0.234 [‡]
	0.22	0.186 [§]	0.081 ^{†‡}	0.087 [†]	0.267 [‡]
100	0.8	0.378 [¶]	0.115 ^{‡§}	0.193 [‡]	0.493 [§]
	0.45	0.376 [¶]	0.094 [‡]	0.140 [‡]	0.470 [§]
	0.22	0.391 [¶]	0.144 ^{‡§}	0.175 [‡]	0.535 [§]
200	0.8	0.864 [*]	0.015 [†]	0.052 [†]	0.878 [¶]
	0.45	0.864 [*]	0.038 [†]	0.141 [‡]	0.901 [¶]
	0.22	0.816 [*]	0.080 [†]	0.277 [‡]	0.897 [¶]

^a Means for each application rate within a column and soil:solution ratio followed by the same symbol are not significantly different at the $P < 0.05$ level using Tukey's test.

^b Undetermined due to small concentration of orthophosphate at or less than detection limit of IC.

In general, the Freundlich parameter α was most influenced by soil:solution ratio (1 : 5 > 1 : 100), followed by amendment rate (inversely proportional to P applied), and then manure type (dairy > poultry > superphosphate). This is demonstrated in Fig. 3, which shows the affect of each amendment at the five different application rates at a soil:solution ratio of 1:100 (Fig. 3), compared to the same soils at a soil:solution ratio of 1:5. Clearly in Fig. 3, the concentration of P sorbed at a soil:solution ratio of 1:100 was less than that at 1:5. In addition, the affect of amendment rate is especially evident at the greatest rate of 200 kg P ha⁻¹, where P sorption (as a negative value indicating desorption) was most affected at the 1:5 soil:solution ratio, and even more so in dairy manure amended soil and extracted solutions, whereas the effect

was much less in the superphosphate amended soil extracted at a soil:solution ratio of 1:100.

4. Discussion

4.1. Solution P fractions

The relative proportion of soil P in inorganic and organic forms can vary from 10% to 90%, however, their relative solubility in soil solution, subsurface flow, and overland flow can also be dramatically different depending largely upon soil chemical conditions. For example, Chardon et al. (1997) found that the application of swine manure containing 46% inorganic P (fresh) for 12 years had enriched soil solution at 70–80 cm deep,

Table 3

Mean concentrations of P fractions in solutions extracted from soils with superphosphate applied

Fertiliser rate (kg P ha ⁻¹)	Filter pore size (µm)	DRP (mg l ⁻¹)	UP (mg l ⁻¹)	DOP (mg l ⁻¹)	Total P (mg l ⁻¹)
<i>1:5 soil:solution ratio</i>					
0	0.8	0.020† ^a	0.120†	0.130†	0.140†
	0.45	0.014†	0.078†	— ^b	0.092†
	0.22	0.016†	0.069†	—	0.085†
25	0.8	0.017†	0.110†	—	0.126†
	0.45	0.020†	0.121†	—	0.140†
	0.22	0.017†	0.123†	—	0.140†
50	0.8	0.023†	0.085†	0.089†	0.109†
	0.45	0.026†	0.075†	0.082†	0.102†
	0.22	0.023†	0.104†	0.108†	0.128†
100	0.8	0.661 ‡	0.066†	0.137†	0.727‡
	0.45	0.618‡	0.080†	0.118†	0.698‡
	0.22	0.488‡	0.191†	0.259†	0.679‡
200	0.8	2.306§	0.037†	0.128†	2.343§
	0.45	2.077§	0.347‡	0.874‡	2.424§
	0.22	2.058§	0.276‡	0.504‡	2.334§
<i>1:100 soil:solution ratio</i>					
0	0.8	0.043†	0.019†	—	0.061†
	0.45	0.014†	0.052†	—	0.066†
	0.22	0.013†	0.063†	—	0.076†
25	0.8	0.320†‡	0.094†	0.384†	0.414†‡
	0.45	0.037†‡	0.150†	—	0.187†‡
	0.22	0.041†‡	0.086†	—	0.126†‡
50	0.8	0.106†‡	0.083†	0.089†	0.189†‡
	0.45	0.091†‡	0.068†	0.074†	0.159†‡
	0.22	0.124†‡	0.045†	0.049†	0.169†‡
100	0.8	0.270‡	0.105†	0.181†	0.376‡
	0.45	0.268‡	0.065†	0.097†	0.333‡
	0.22	0.261‡	0.082†	0.099†	0.343‡
200	0.8	0.475§	0.096†	0.362†	0.572§
	0.45	0.466§	0.032†	0.108†	0.498§
	0.22	0.466§	0.152†	0.323†	0.618§

^a Means for each application rate within a column and soil:solution ratio followed by the same symbol are not significantly different at the $P < 0.05$ level using Tukey's test.

^b Undetermined due to small concentration of orthophosphate at or less than detection limit of IC.

Table 4

Mehlich-3 extractable P in each of the 15 soils used after 5 years of P amendment applications

Amendment rate (kg P ha ⁻¹)	P Amendment		
	Dairy manure	Poultry manure	Superphosphate
0	12 ± 1 ^a	14 ± 1	9 ± 2
25	17 ± 2	14 ± 3	24 ± 3
50	48 ± 4	19 ± 5	26 ± 4
100	65 ± 4	63 ± 4	47 ± 5
200	173 ± 5	156 ± 5	180 ± 5

^a Standard error of the mean.

yielding a dissolved organic P proportion of 90%, compared to 10% at the soil surface. Conversely, McDowell and Sharpley (2001b) showed that the ap-

plication of dairy manure (containing 25% organic P) had relatively little organic P leaching, immediately after and 1 year after application (<10% of total P leached). Clearly, the loss of P in inorganic and organic forms is a characteristic driven by the nature and properties of the soil.

In the current study, the greatest concentration of water extractable organic P was generally in the dairy manured soils, followed by soils with poultry manure applied, and then superphosphate. Soils that have been recently amended with dairy manure and poultry litter can show large amounts of UP lost in both subsurface and overland flow (Edwards and Daniel, 1992; Smith and Jackson, 1998). Sharpley and Moyer (2000) found that on a wet-weight basis, the leaching of organic P was far greater from dairy manure than poultry manure, although the total amount of P leached (inorganic and

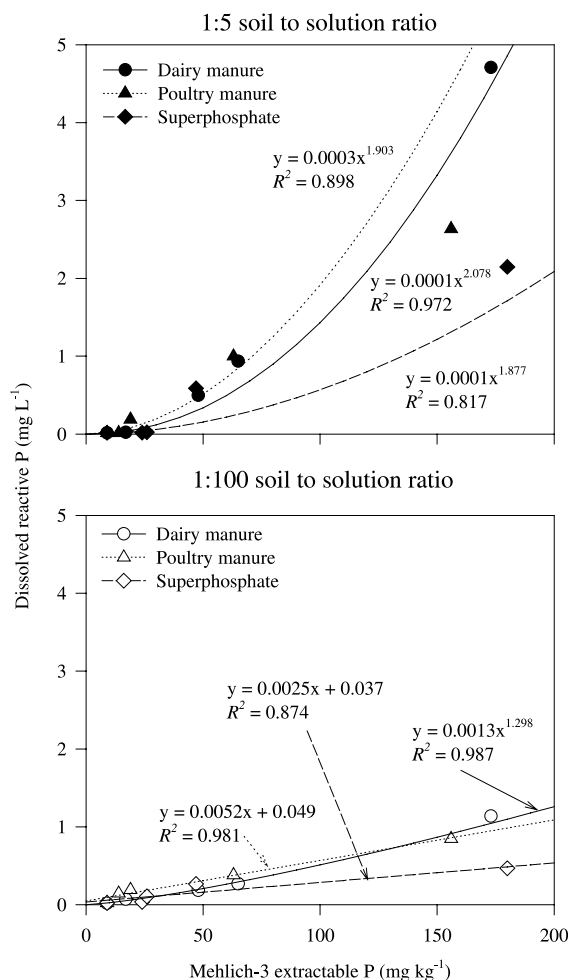


Fig. 1. The relationship between DRP extracted at soil:solution ratios of 1:5 and 1:100 and Mehlich-3 extractable P for each amendment type.

organic) was greater from poultry than dairy manure. The authors found that the proportion of P potentially available for leaching could be estimated from a water extraction (of the manure).

In addition, McDowell and Sharpley (2001a) found that the P release relative to soil test P (e.g., Mehlich-3 extractable P) could also be estimated with a water extraction (of the soil). These authors also noted that the behaviour of P in runoff would be better predicted at soil:solution ratios of overland flow closer to the suspended sediment to solution ratio; a hypothesis proposed by Ryden et al. (1973). With this in mind, the relative proportions of inorganic P (DRP) to organic P (DOP) extracted from the Hagerstown soil in the present study, were significantly different between the two ratios employed, organic P appearing to be more soluble in the 1:100 ratio than the 1:5 ratio. This was expressed even

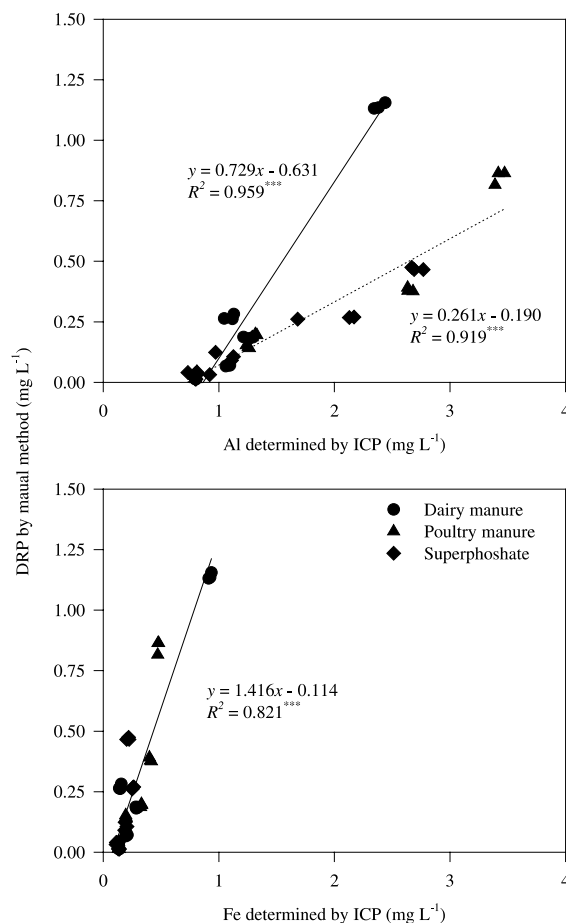


Fig. 2. The relationship between DRP determined by the method of Murphy and Riley (1962) and total Al concentration in soil solution (at soil:solution ratios of 1:5 and 1:100) as determined by ICP-MAS.

with increased amendment rates, and hence decreased proportions of organic P relative to inorganic P.

Even in systems where P is applied as inorganic fertilisers, organic forms of P can contribute a significant proportion of the total P lost in subsurface or overland flow. For example, Turner and Haygarth (2000b) showed that a fertiliser application rate of 40 kg P ha^{-1} yielded from 29% to 38% of total P as unreactive P (UP: largely organic P) in subsurface flow from lysimeters of four different soils.

The relative behaviour of inorganic and organic P as a function of Mehlich-3 extractable P is important from an environmental standpoint, since DOP is in some circumstances considered bioavailable to aquatic plants (Heathwaite et al., 1997). The data clearly showed two opposite trends for DRP and DOP against Mehlich-3 extractable P. Dissolved reactive P expressed a typical quantity (Mehlich-3 extractable P) intensity (DRP)

Table 5

Mean percent solubilised P for each manure type and application rate in excess of 25 kg P ha⁻¹ for each ratio and filter size

Application rate and filter size (µm)	Extraction ratio	Dairy manure	Poultry manure	Superphosphate
<i>50 kg P ha⁻¹</i>				
0.8	1:5	70† ^a	65†	— ^b
	1:100	71†	73†	—
0.45	1:5	58‡	49‡	—
	1:100	62‡	64†	—
0.22	1:5	64‡	38‡	—
	1:100	64‡	47‡	—
<i>100 kg P ha⁻¹</i>				
0.8	1:5	51†	76†	52†
	1:100	71‡	40‡	42†
0.45	1:5	41†	48†	32‡
	1:100	61‡	33‡	33‡
0.22	1:5	36†	30‡	26‡
	1:100	63‡	17‡	17‡
<i>200 kg P ha⁻¹</i>				
0.8	1:5	46†	66†	71†
	1:100	25†	72†	73†
0.45	1:5	16‡	61†	60†‡
	1:100	17‡	73†	71†
0.22	1:5	18‡	43‡	45‡
	1:100	18‡	71†	53‡

^a Means for each application rate followed by the same symbol are not significantly different at the $P < 0.05$ level using Turkey's test.^b Solubilised P cannot be determined due to orthophosphate concentrations less than the ion chromatography detection limit. This also applies for soils amended at rates of 25 kg P ha⁻¹ or less.

relationship (McDowell et al., 2001), with DRP increasing at a much greater rate relative to Mehlich-3 extractable P at high Mehlich concentrations (ca. >50 mg P kg⁻¹). However, DOP exhibited the exact opposite relationship relative to Mehlich-3 extractable P, implying that during environmental analysis of soils with a low Mehlich-3 concentration, organic P should not be underestimated or determined incorrectly.

4.2. Method of analysis

Using the method of Murphy and Riley (1962), measures of DRP can differ due to the hydrolysis of organic P, desorption of P from particulates, and interferences from ions such as arsenate (AsO₄), silicate (SiO₄), and organic compounds such as citrate and oxalate. Variations of this method have improved the detection limit and accuracy, however, ion chromatography is seen as a method relatively free of these problems and yet accurate (although its detection limit is currently not as good as manual methods) (Gerke, 1992). Using ion chromatography, DOP was calculated as the difference between DRP detected by ion chromatography and TDP, whereas UP is the difference between DRP detected by the method of Murphy and Riley (1962) and TDP. The fact that UP is greater in all cases than DOP, shows that hydrolysis and/or desorp-

tion from particles is/are occurring. This fraction, expressed as a percentage of DOP, shows that from 16% to 73% of organic P is being hydrolysed or generated by difference due to desorption. On a percentage basis, no significant difference was noted between the values of solubilised P in the two soil:solution ratios.

A significant difference was noted between the percentage of P solubilised after filtration through a 0.8 µm filter and that filtered through a 0.45 or 0.22 µm filter. Since no difference is noted between filtration at 0.45 and 0.22 µm, it is likely that the discrepancy between the two methods of DRP detection is caused by the desorption of P from particles < 0.8 µm but > 0.45 µm.

Phosphorous that is solubilised during analysis by the manual method may originate from many forms such as colloids, oxides, and humic substances which are in the range of 0.01 or smaller to 5.0 µm. Sinaj et al. (1998) hypothesised that some may arise from the dissolution of Ca-phosphates, extracted from a calcareous soil (Xerochrept). However, the authors noted a distinct negative correlation between the rate of recovery from a sample spiked 24 h before analysis and the Al concentration.

In the present study, using ICP to determine total Al, Ca, Fe, and Mg in each of the solutions, a positive relationship was found between the concentration of P

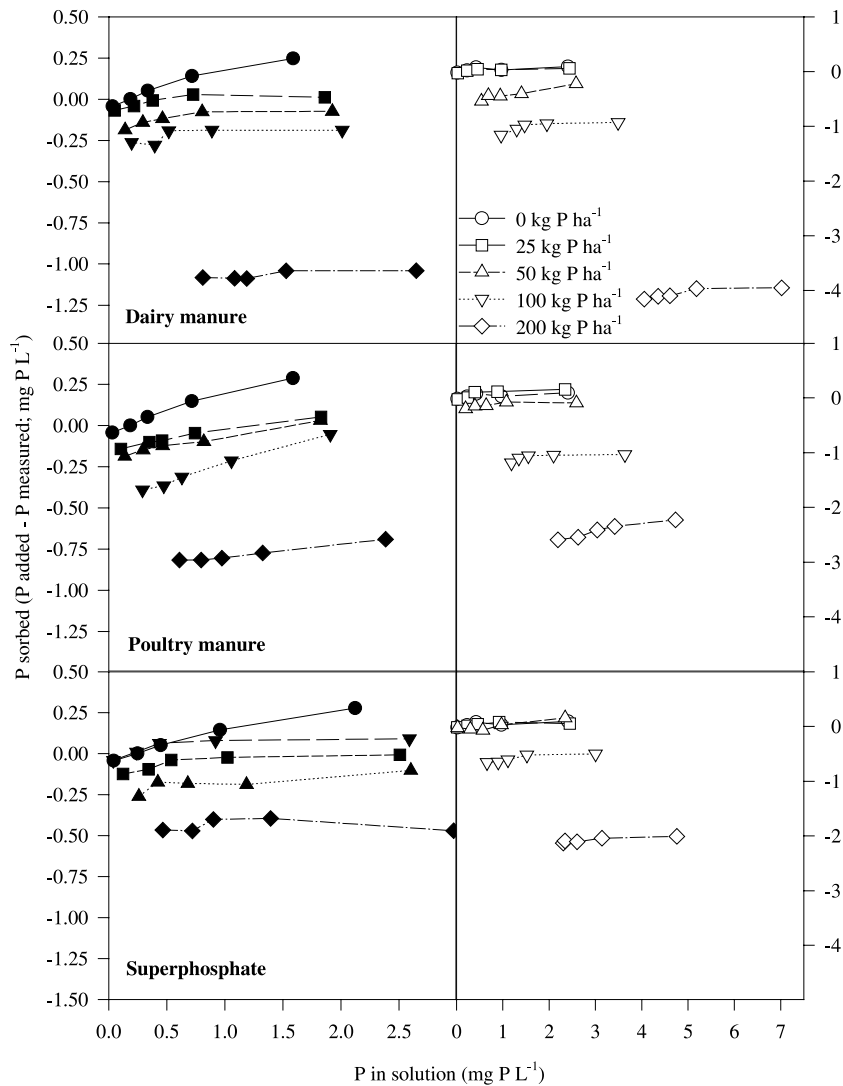


Fig. 3. Quantity–intensity relationship as P sorbed (negative values = desorption) vs. P measured in solution (both determined manually) for solutions extracted from soils at a soil:solution ratio of 1:100 and filtered at $<0.22 \mu\text{m}$ (closed symbols) and at a ratio of 1:5 and filtered at $<0.8 \mu\text{m}$ (open symbols).

and either Al or Fe in solution, but not Ca or Mg. This implies that Ca- and Mg-phosphates play little or no role in determining total P concentrations in these soil solutions and that total P is linked to the dissolution of Al- and Fe-phosphates, whether inorganic (colloidal) or organic (humic) in origin. Similarly, Gerke (1992) concluded that the presence of up to 50% of DOP as humic–Al–(Fe–) complexes might account for acid hydrolysis of P in soil solution from four sandy soils.

In our study, more P was determined as hydrolysed or desorbed P for soils amended with superphosphate than with manure (Table 5). This implies that the or-

ganic fraction derived from manures may be either recalcitrant or certainly less desorbable compared to that derived from superphosphate. Indeed, Weaver (1997) showed that significantly more superphosphate accumulated in labile soil P fractions (e.g., water, Fe-oxide strip, or bicarbonate soluble P commonly associated with Al and/or Fe oxides) compared to either dairy or poultry manure amended soils. However, we also know that manure application causes the soil to disperse, thereby increasing the possibility that colloids may contribute to solubilised P in manured soil extracts. The relative effect of this is unclear, but some information may be gained by examining the sorption–desorption

properties of the solutions in response to P additions of various concentrations.

4.3. Sorption of P in solution

The sorption or desorption of P in soils is known to be affected by the amount and type of organic matter (McDowell and Condron, 2001). Sinaj et al. (1998) found that P measured by ion chromatography from a solution spiked with P 24 h previously, varied from 69% in a Haplustox to 95% in a Paleustalf. Clearly P sorbed by colloidal constituents in solution varies as a function of soil type and kinetics. In our study, quantity–intensity diagrams for P sorbed in solution (Fig. 3) show P sorption occurred in all soil solutions from soils that had received no amendments, an amendment rate of 25 kg P ha⁻¹, and in the soil amended with 50 kg P ha⁻¹ superphosphate (P sorbed ≥ 0 mg l⁻¹). The greater sorption of P in soils amended with superphosphate than dairy manure can be explained by the saturation (by competitive sorption) of sorption sites by organic matter (McDowell and Condron, 2001). This also infers that organic constituents, possibly Al-humic-P complexes, greatly affected P sorption in our soil solutions. Such compounds are known to exist in solution. For example, Jones et al. (1993) found that by adding ³²P-labelled orthophosphate to lake water, the molecular weight of P-containing compounds greatly increased by co-precipitation with Fe-containing compounds. Haygarth et al. (1997) found that a significant proportion of P in river waters, surface runoff, or leachate can be in the <0.45 μ m to >1000 MW range as colloidal organic P complexes, which could represent a source of mobile and bioavailable P (in overland flow or macropore flow). Clearly, further investigation of these organic-P components in soil solution is warranted.

While P sorption–desorption was greatly affected by soil amendment rate and soil:solution ratio, no clear significant difference could be made between filter sizes. This infers that colloids play a minimal role in affecting P concentrations in these soil solutions and that sorption may be accounted for by the formation of non-hydrolysable or detectable P-containing compounds (using the method of Murphy and Riley, 1962). This contrasts with Sinaj et al. (1998) who advocated the use of <0.22 μ m filtration to eliminate any sorption effects during storage and/or analysis. Jenkins (1968), on the other hand, advocates the use of <0.45 μ m filtration for waters. Clearly, the level of filtration required is dependent upon the aggregate stability of the soil and its ability to slake into many small particles that may cause P determination to vary. In our study, no recommendation could be made to use filtration at 0.22 μ m, or indeed 0.45 μ m, as opposed to filtration through a 0.8 μ m filter, based on sorptive properties alone. However, as was evident from the significant difference between 0.45 μ m (or less) fil-

tration and 0.8 μ m filtration on the organic P fraction and its determination, it is clear that filtration at 0.45 μ m (or less) is required to accurately fractionate P.

5. Conclusions

Results demonstrate that the proportion of P distributed between inorganic (DRP) and organic P (DOP or UP) fractions is greatly affected by the rate and type of amendment. As expected, a greater concentration of P was extracted using a soil:solution ratio of 1:5 compared to 1:100. However, the solubility of organic P appeared to be greater in the wider ratio. Overall, DRP was the dominant fraction in all soils, however, the relative proportion of DRP to DOP decreased as the rates of P amendment increased. Relative to Mehlich-3 extractable P, DRP exhibited a power relationship and UP the opposite. However, this was less evident and resulted in a linear relationship at the 1:100 soil:solution ratio and was attributed to the expression of the soils buffer capacity at the two ratios. Clearly, the risk of DOP (especially if easily hydrolysed) at low concentrations of soil test P should not be underestimated, just as much as the greater risk of orthophosphate movement at concentrations in excess of ca. 50 mg Mehlich-3 P kg⁻¹ (for this soil) should not be overlooked.

Detection of DRP was on average 12.5% greater than P detected by ion chromatography. A linear relationship was found between total Al and P in solution, which could act as a mechanism of overestimation via the acid mediated hydrolysis of Al-humic-P substances. Additional overestimation from acid mediated desorption of P from colloids could not be discounted. However, no difference in solubilised P could be detected between solutions filtered at 0.22 and at 0.45 μ m, and furthermore no difference occurred between any of the filter sizes and their effect on P sorption, inferring the effect of colloids on solution P dynamics was minimal. There was a clear effect of amendment type on the potential for overestimation. Organic P from manured soils was more recalcitrant to hydrolysis compared to DOP derived from superphosphate and attributed to their relative accumulation in non-labile and labile pools, respectively.

Sorption of P by solutions was greatly affected by the rate of amendment and the ratio of the soil:solution extraction. More P was sorbed by superphosphate compared to dairy manure and attributed to the saturation of sites by organic matter or the formation of non-hydrolysable or non-detectable (using the method of Murphy and Riley, 1962) P-containing compounds. In order to minimise the effects of colloids on P dynamics and the potential for organic P hydrolysis in solution, filtration to at least 0.45 μ m is required. However, it is recognised that this is soil specific and

soils with a lesser aggregate stability and more prone to slaking may require additional filtration.

References

- Aiken, G., Jeener, J., 1993. Isolation and characterization of dissolved and colloidal organic matter. *Chemistry and Ecology* 8, 135–151.
- Blomqvist, S., Hjelström, K., Sjösten, A., 1993. Interference from arsenate, fluoride and determining phosphate in water by the phosphoantimonymolybdenum blue method. *International Journal of Environmental Analytical Chemistry* 54, 31–43.
- Cai, T.T., Yost, R.S., Olsen, T.W., 1994. Potential errors in the use of the Murphy and Riley method for determination of phosphorus in soil extracts. *Communications in Soil Science and Plant Analysis* 25, 3129–3146.
- Chardon, W.J., Oenema, O., Castilho, P., Vriesema, R., Japenga, J., Blaauw, D., 1997. Organic phosphorus in solutions and leachates from soils treated with animal slurries. *Journal of Environmental Quality* 26, 372–378.
- Ciavatta, C., Antisari, L.V., Sequi, P., 1990. Interference of soluble silica in determination of orthophosphate-phosphorus. *Journal of Environmental Quality* 19, 761–764.
- Denison, F.H., Haygarth, P.M., House, W.A., Bristow, A.W., 1998. The measurement of dissolved phosphorus compounds: evidence for hydrolysis during storage and implications for analytical definitions in environmental analysis. *International Journal of Environmental Analytical Chemistry* 69, 111–123.
- Edwards, D.R., Daniel, T.C., 1992. Potential runoff quality effects of poultry manure slurry applied to fescue plots. *Transactions of the American Society of Agricultural Engineers* 35, 1827–1832.
- Frossard, E., Stewart, J.W.B., St. Arnaud, R.J., 1989. Distribution and mobility of phosphorus in grassland and forest soils of Saskatchewan. *Canadian Journal of Soil Science* 69, 401–416.
- Gerke, J., 1992. Orthophosphate and organic phosphate in the soil solution of four sandy soils in relation to pH-evidence for humic-Fe-(Al-) phosphate complexes. *Communications in Soil Science and Plant Analysis* 23, 601–612.
- Gerke, J., Jungk, A., 1991. Separation of phosphorus bound to organic matrices from inorganic phosphorus in alkaline soil extracts by ultrafiltration. *Communications in Soil Science and Plant Analysis* 22, 1621–1630.
- Haygarth, P.M., Ashby, C.D., Jarvis, S.C., 1995. Short-term changes in the molybdate reactive phosphorus of stored soil waters. *Journal of Environmental Quality* 24, 1133–1140.
- Haygarth, P.M., Warwick, M.S., House, W.A., 1997. Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. *Water Research* 31, 439–448.
- Heathwaite, A.L., Griffiths, P., Haygarth, P.M., Jarvis, S.C., Parkinson, R.J., 1997. Phosphorus loss from grassland soils: implications of land management for the quality of receiving waters. In: *Freshwater Contamination, Proceedings Rabat Symposium, April–May 1997*, IHAS Publication No. 243, pp. 177–186.
- Holford, I.C.R., 1982. The comparative significance and utility of the Freundlich and Langmuir parameters for characterizing sorption and plant availability of phosphate in soils. *Australian Journal of Soil Research* 20, 233–242.
- Jenkins, D., 1968. The differentiation, analysis and preservation of nitrogen and phosphorus in natural waters. *Advances in Chemistry Series* 13, 265–280.
- Jones, R.I., Shaw, P.J., De Haan, H., 1993. Effects of dissolved humic substances on speciation of iron and phosphate at different pH and ionic strength. *Environmental Science and Technology* 27, 1052–1059.
- McDowell, R.W., Condon, L.M., 2000. Chemical nature and potential mobility of phosphorus in fertilized grassland soils. *Nutrient Cycling in Agroecosystems* 57, 225–233.
- McDowell, R.W., Condon, L.M., 2001. Influence of soil constituents on soil phosphorus sorption and desorption. *Communications in Soil Science and Plant Analysis* (in press).
- McDowell, R.W., Sharpley, A.N., 2001a. Approximating phosphorus release to surface runoff and subsurface drainage. *Journal of Environmental Quality* 30, 508–520.
- McDowell, R.W., Sharpley, A.N., 2001b. Phosphorus losses in subsurface flow before and after manure application to intensively farmed land. *The Science of the Total Environment* (in press).
- McDowell, R.W., Sharpley, A.N., Condon, L.M., Haygarth, P.M., Brookes, P.C., 2001. Processes controlling soil phosphorus release to runoff and implications for agricultural management. *Nutrient Cycling in Agroecosystems* (in press).
- Mehlich, A., 1984. Mehlich-3 soil test extractant: a modification of Mehlich-2 extractant. *Communications in Soil Science and Plant Analysis* 15, 1409–1416.
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 27, 31–36.
- Vaz, M.D., Edwards, A.C., Shand, C.A., Cresser, M.S., 1993. Phosphorus fractions in soil solution: influence of soil acidity and fertiliser additions. *Plant and Soil* 148, 175–183.
- Ryden, J.C., Syers, J.K., Harris, R.F., 1973. Phosphorus in runoff and streams. *Advances in Agronomy* 25, 1–45.
- Sharpley, A.N., Moyer, B., 2000. Phosphate forms in manure and compost and their release during simulated rainfall. *Journal of Environmental Quality* 29, 1462–1469.
- Sinaj, S., Mächler, F., Frossard, E., Faisse, C., Oberson, A., Morel, C., 1998. Interference of colloidal particles in the determination of orthophosphate concentrations in soil water extracts. *Communications in Soil Science and Plant Analysis* 29, 1091–1105.
- Smith, K.A., Jackson, D.R., 1998. Phosphorus in run-off following manure applications to arable land. In: Foy, R.H., Dils, R. (Eds.), *Practical and innovative measures for the control of agricultural phosphorus losses to water*. OECD Workshop, Department of Agriculture, Northern Ireland, Belfast, Northern Ireland, pp. 126–127.
- Snedecor, G.W., Cochran, W.G., 1991. *Statistical Methods*, eighth ed. Iowa State University Press, Ames, Iowa.
- SPSS Inc., 1999. *SPSS User's Manual*, version 10.0. Chicago, IL, USA.
- Taylor, M.D., 2000. Determination of total phosphorus in soil using simple Kjeldahl digestion. *Communications in Soil Science and Plant Analysis* 31, 2665–2670.

- Turner, B.L., Haygarth, P.M., 2000a. Phosphorus forms and concentrations in leachate under four grassland soil types. *Soil Science Society of America Journal* 64, 1090–1099.
- Turner, B.L., Haygarth, P.M., 2000b. Organic phosphorus characterisation by phosphatase hydrolysable phosphorus techniques: applications to soil extracts and runoff waters. In: Whitton, B.A., Hernández, I. (Eds.), *Phosphatases in the Environment*. Kluwer Academic Publishers, The Netherlands, in press.
- Weaver, S.R., 1997. Effects of manure and compost as sources of phosphorus on soil P fractions. M.Sc. Thesis, The Pennsylvania State University, unpublished.